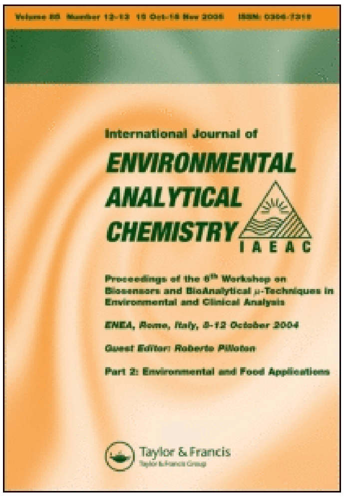

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New Assessments on CFCs Tropospheric Concentration Levels Measured in Terra Nova Bay (Antarctica)

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NEW ASSESSMENTS ON CFCs TROPOSPHERIC CONCENTRATION LEVELS MEASURED IN TERRA NOVA BAY (ANTARCTICA)

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Data concerning tropospheric levels of some chlorofluorocarbons and other halogenated hydrocarbons are reported. These are referred to atmospheric samples collected during the 1993/94 Austral Summer Antarctic Campaign in Terra Nova Bay. Samples collected in Stainless Steel canisters were analyzed in our laboratory by gas chromatography-electron capture detection (GC-ECD). A comparison with data obtained in previous campaigns is reported as well.

KEY WORDS: Chlorofluorocarbons, atmosphere, Antarctica, GC-ECD.

INTRODUCTION

As already stated in some previous papers[1-4], the intent of this research work is to give data on the tropospheric levels of selected man-made C_1-C_2 halogenated hydrocarbons, whose fundamental role in the Global Change is well known. Compounds that are object of this study are: $CFCl_3$ (F11), CF_2Cl_2 (F12), $C_2F_3Cl_3$ (F113), $C_2F_4Cl_2$ (F114), CH_3CCl_3 and CCl_4. Their involvement in the Global Change is a double one: they are responsible both for stratospheric ozone layer depletion, and for "greenhouse effect". The capability of these compounds to destroy stratospheric ozone has been widely demonstrated[5-7]. As a consequence, they have been listed in the "Montreal Protocol"[8] as the most dangerous substances for the ozone layer. The Protocol, and subsequent amendments, required developed countries to eliminate CFCs production by 1996.

The involvement of CFCs in the "greenhouse effect" is due to their strong ability to absorb, in the range of the "atmospheric window", IR radiation emitted by the earth surface, even though their atmospheric levels are relatively low if compared with those of major "greenhouse gases" (CO_2 and CH_4). Furthermore, their percentage annual growth is much greater than that of CO_2 and CH_4. On this basis, it could be hypothesized that, by the end of this century, CFCs could become the main responsible factor, after CO_2, for the "greenhouse effect"[9].

For these reasons, data concerning tropospheric levels of the aforementioned compounds in a remote region, distant from their major emission sources, are very important. In fact, the average global concentration of these compounds can be calculated, and their secular trend of growth rates estimated. In this frame, Antarctica can be positively considered as the ideal site for these kind of measurements.

In the present paper, data concerning the 1993–94 Austral Summer Antarctic Campaign, which took place within the Italian Research Programme in Antarctica, are reported, and they are compared with those obtained during the past campaigns. Furthermore, some modifications have been introduced to simplify the sampling and analytical procedures.

EXPERIMENTAL

Sampling. As the only source of local contamination can be ascribed to the Italian Station activity, the choice of sampling sites was made based on their distance from Terra Nova Bay Station (Ross Sea Region, Northern Victoria Land, Antarctica); all sites were at least 30 Km away from the Italian Station, as shown in Figure 1.

During the 1993–94 Austral Summer campaign air samples were collected in 0.85 and 16 L Stainless Steel canisters[10] (Biospheric Research Corporation, Hillsboro, OR, USA), whose internal walls were electropolished to provide a chromo-nickel oxide skin, which makes inactive the surface. As CFCs are particularly inert, they are stable in canisters for several months.

Air was drawn inside the canisters by means of a portable ultra-clean air pump (model FC-1121, Biospheric Research Corporation, Hillsboro, OR, USA), whose air contact surfaces were all in Stainless Steel, in order to eliminate any release of organic compounds. Gas-tight connections between the canister and the pump were assured by two Nupro valves (Nupro Co., Willoughby, OH, USA) and a purge-tee fitted with a pressure gauge.

In Figure 2 a diagram of the sampling apparatus is shown. Air was drawn inside the canister at a pressure of 3 atm., and flushed several times, to assure a complete washing, before the final sampling. Then canisters were tightly closed and stored at room temperature before the analysis performed in our laboratory.

Sample introduction into the GC unit. Samples, collected with the above described procedure, were analyzed in gas chromatography with an Electron Capture Detection (ECD). As ECD is a very sensitive detector towards halogenated compounds, no preconcentration step is needed when F12, F11, F113, CH_3CCl_3 and CCl_4, whose atmospheric concentrations are adequate to detector sensitivity, have to be determined. Air samples were introduced into the gas chromatographic unit by means of a conventional six-port valve (Valco Instrument Inc., Houston, TX, USA) system, as described elsewhere[11].

When F114, whose atmospheric levels are relatively low, has to be analyzed, a pre-concentration step is needed. A measured volume (0.5 L) of air from the canister is passed through a trap made with a glass tubing (10 cm long, 0.3 cm I.D.) filled with 230 mg of Carbotrap 1 60–80 mesh (Alltech, Deerfield, IL, USA). During the enrichment step, due to the low break through volume of F114 at room temperature, the trap is kept at the temperature of –70°C by means of dry ice. After this step, trap is connected to the GC by a four-port valve. When the trap is not in line with the gas chromatograph, it is heated in a home-made oven for two minutes at 270°C, then the valve is switched and the desorbed analytes are transferred by the carrier gas into the GC column[12–13].

Gas chromatographic analysis. The GC-ECD unit was a DANI 8521-a (DANI Strumentazione Analitica SpA, Monza, Italy) equipped with a glass column (2 m long,

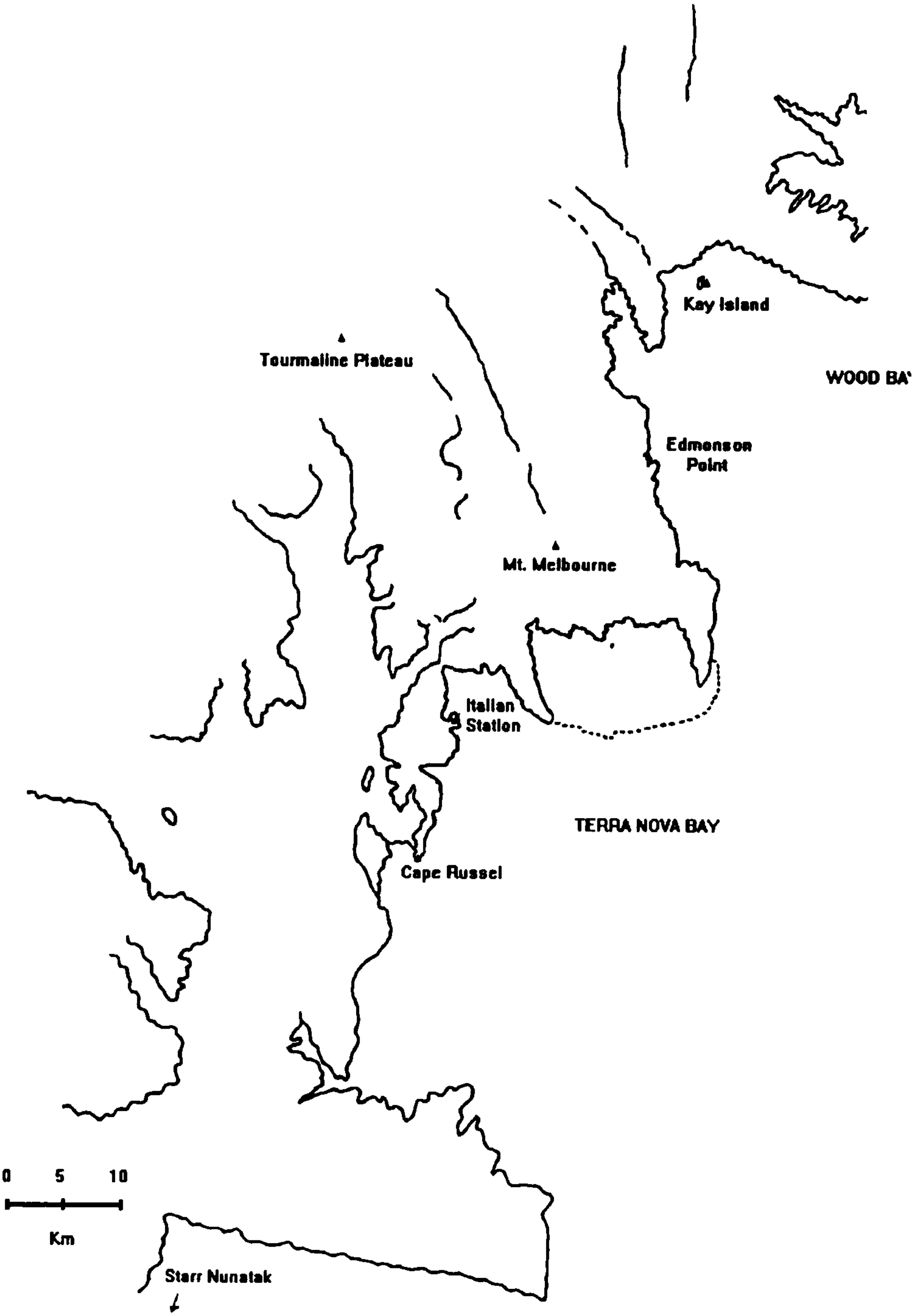

Figure 1 Sampling sites location, 1993–94 campaign.

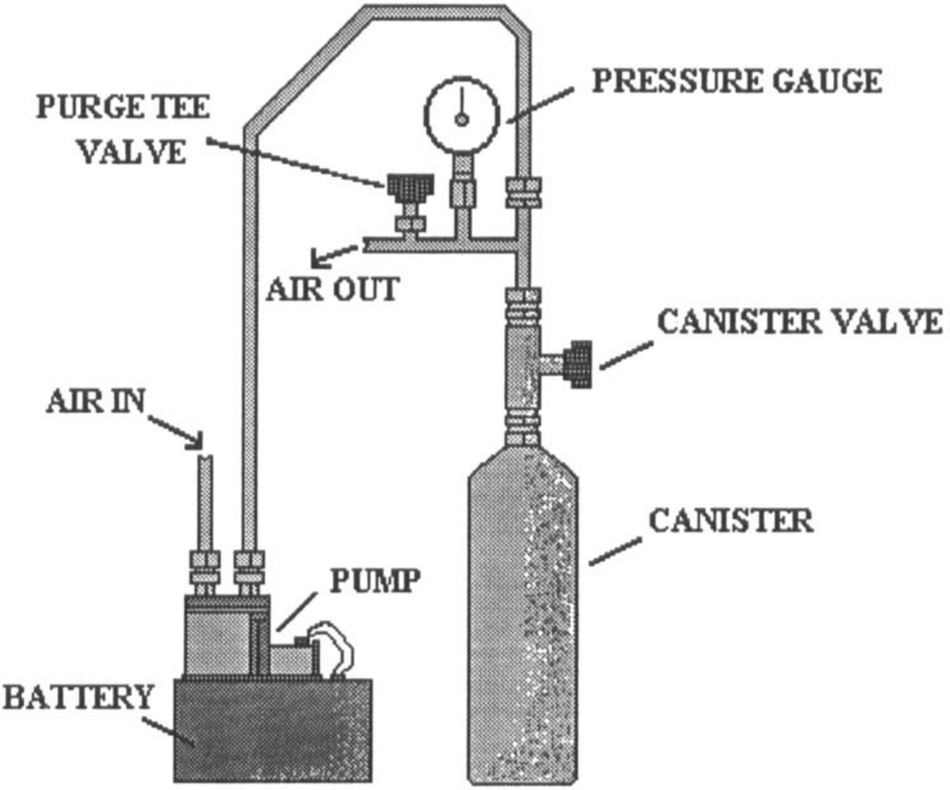

Figure 2 Diagram of the sampling apparatus.

0.2 cm I.D.) packed with Carbograph 1 (Alltech, Deerfield, IL, USA) coated with 1% SP1000 (Supelco, Bellefonte, PA, USA). The temperature programme was: 4 min. at 40°C, then 4°C/min to 120°, hold 1 minute, then 20°C/min to 180°C, hold 15 minutes. UHP Nitrogen was used as carrier gas.

In Figure 3 a chromatogram obtained analyzing a 2.5 mL air sample collected in Antarctica with the direct injection procedure is shown.

Quantification was performed by comparing the actual sample chromatogram with one obtained analyzing a 2.5 mL of a standard mixture of the compounds of interest generated by means of home-made Teflon FEP permeation tubes[14]. The concentration of each compound in the standard solution is close to that of the actual sample, and anyway within the linear range of the calibration curves.

RESULTS AND DISCUSSION

In the past years, our group had set up a sophisticated analytical procedure[12,13] for the analysis of CFCs in the atmosphere of both industrialized and remote areas. This procedure makes use of a high resolution mass spectrometer used in the selected ion monitoring (SIM) mode as a specific detector, and of thermally desorbed traps for

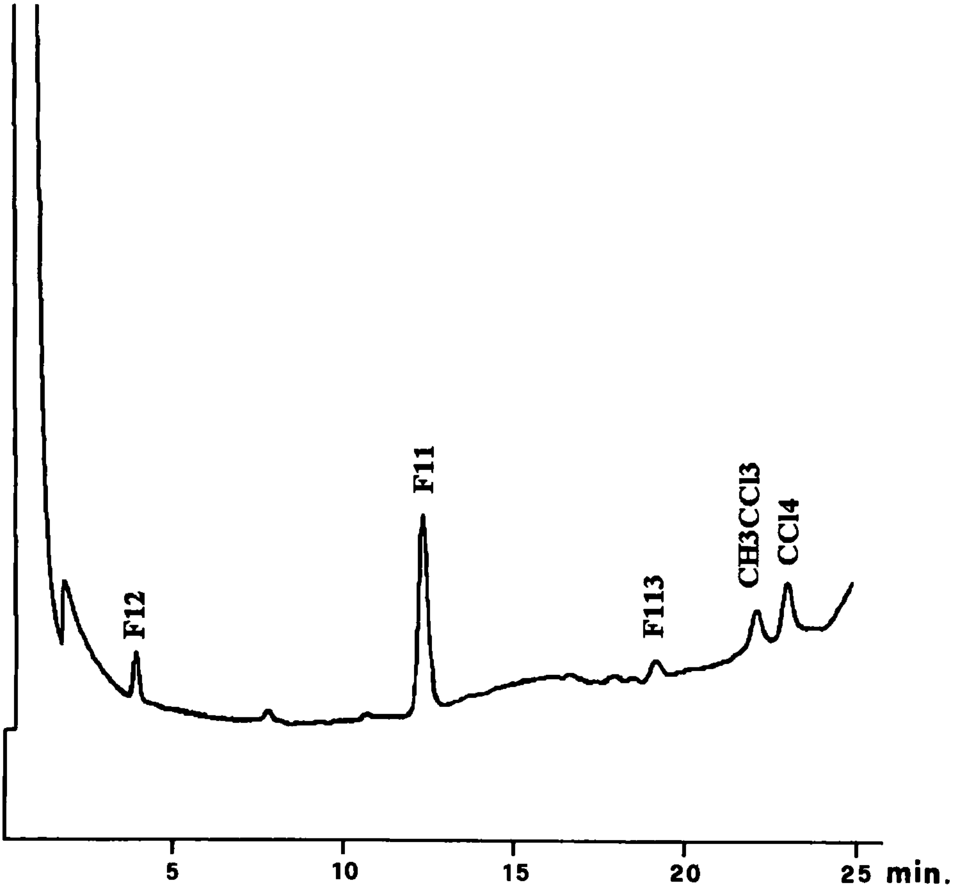

Figure 3 Gas chromatogram obtained after direct injection of 2.5 mL of air collected in Antarctica during the 1993/94 campaign. For chromatographic conditions, see text.

sampling. In this way trace compounds[15] could be detected and interferences due to oxygenated or double bonds containing compounds could be eliminated.

After several years of experience in remote areas[1-4], we decided, due to the purity of Antarctic atmosphere, and on the basis of comparative results obtained using MS and EC detection, that the analysis in remote areas, such as Antarctica, could be performed by using EC detection and canister sampling.

The canister sampling procedure is much easier than the one which makes use of enrichment traps, and this fact is not negligible when operating in severe climatic conditions. Furthermore, each sample could be analyzed several times in order to test the repeatability of the overall analytic method. In this case at least six samples (2.5 mL volume) from each canister were analyzed. Finally canisters showed to be positively inert towards most of the compounds of interest for a relatively long time, meanwhile contamination problems might occur when storing enrichment traps for several weeks.

In Table 1, data obtained analyzing samples collected in six different sampling stations during the 1993–94 Antarctic Campaign are reported. As expected, no appreciable differences in CFCs concentration levels in the different stations were found.

Table 1 Halocarbon concentrations measured in six different sampling sites expressed in ppt (10^{-12} v/v).

Station	*F12*	*F114*	*F11*	*F113*	*CH_3CCl_3*	*CCl_4*
Tourmaline Plateau 74°08' S–163°26'E	524 ± 7%	26 ± 10%	312 ± 9%	97 ± 9%	149 ±14%	108 ±15%
Mount Melbourne 74°20' S–163°20' E	522 ± 6%	24 ± 9%	313 ± 8%	86 ± 8%	182 ± 12%	114 ± 16%
Cape Russel 74°55' S–163°50' E	516 ± 6%	23 ± 11%	292 ± 4%	80 ± 9%	152 ± 11%	130 ± 12%
Starr Nunatak 75°54' S–162°33' E	504 ± 5%	27 ± 12%	313 ± 5%	98 ± 11%	188 ± 10%	102 ± 17%
Edmonson Point 74°20' S–165°07' E	502 ± 9%	21 ± 10%	305 ± 10%	81 ± 12%	150 ± 16%	105 ± 14%
Kay Island 74°04' S–165°19' E	503 ± 3%	22 ± 9%	311 ± 7%	80 ± 7%	161 ± 13%	112 ± 18%

In Table 2, mean values are reported together relative standard deviations calculated on six samples.

In Figure 4 the plotting of F12, F11, F113 and CH_3CCl_3 concentrations measured during four past Antarctic campaigns against time (years) is shown. The gap in the record during 1991–93 was due to a lack of air samples.

These plots show that, at the moment, a flattening of the concentration levels ascribed to the restriction policies concerning CFCs production and consumption adopted by developed countries further to the "Montreal Protocol", is not so evident as it is in the northern hemisphere.

Data concerning concentration levels of compounds like F14 and F113, whose measurements in the southern hemisphere are rare, are particularly interesting. Anomalous data concerning carbon tetrachloride levels could probably be ascribed to the fact that this compound is the most reactive, and some decomposition problems might occur.

Table 2 Mean halocarbon concentrations in Antarctic trosposphere, 1993/94 campaign.

Compounds	*ppt (10^{-12} v/v)*
F12	512 ± 2%
F114	24 ± 1%
F11	307 ± 2%
F113	87 ± 2%
CH_3CCl_3	163 ± 2%
CCl_4	111 ± 2%

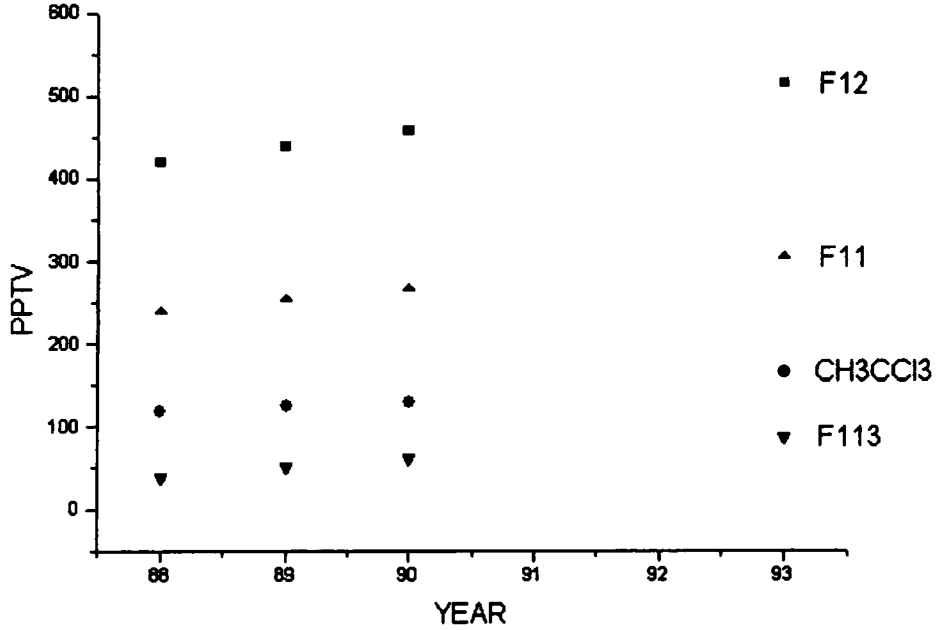

Figure 4 Selected halocarbons concentration levels plotted against time (years).

Acknowledgements

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